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A STUDY OF ORGANIC CHEMICAL REACTIONS IN MICROEMULSIONS
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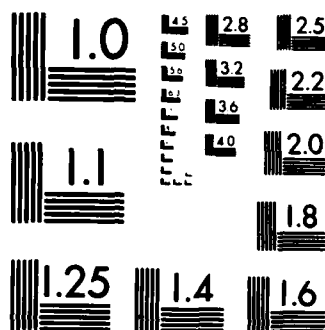
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KEY WORDS (Continue on reverse side if necessary and identify by block number)

microemulsions, organic synthesis
microemulsions, reactive site
microemulsion, destructible (cleavable) surfactant-based
destructible (cleavable) surfactants
turnover catalysts

ABSTRACT (Continue on reverse side if necessary and identify by block number)

This Final Report summarizes the work performed under the contract noted above. Three different aspects of the application of microemulsions in organic synthesis were investigated. The first involved a delineation of the ability of microemulsions to catalyze synthetically useful reactions of water-insoluble organic compounds with water-soluble inorganic reagents. The second aspect involved an identification of the reactive site for such

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20. Abstract (continued)

reactions. The third encompassed the synthesis of destructible (cleavable) surfactants, a new class of surfactants specifically tailored for the use of microemulsions in organic synthesis. We also began the design and synthesis of turnover catalysts for carbon and phosphorus ester hydrolysis. *Original or*

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A Study of Organic Chemical Reactions in Microemulsions

Final Report

by

David A. Jaeger

October 24, 1984

U. S. Army Research Office

Contract No. DAAG29-81-K-0100

Department of Chemistry

University of Wyoming

Laramie, Wyoming 82071

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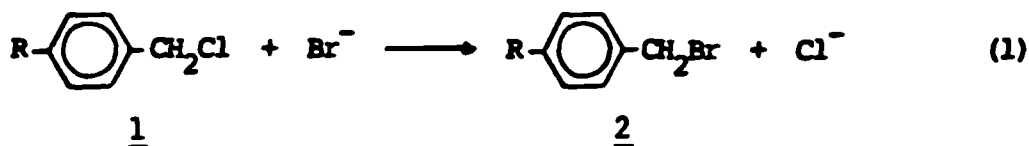
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I. Statement of the Problem Studied

We have investigated several different aspects of the application of microemulsions (μ E's) in organic synthesis. The first involved a delineation of the ability of μ E's to catalyze synthetically useful reactions of water-insoluble organic substrates with water-soluble inorganic reagents under homogeneous conditions, and the second, identification of the reactive site for such reactions. A priori, there are three limiting reactive sites: oil pseudophase, aqueous pseudophase, and interphase. The third aspect encompassed the synthesis of destructible (cleavable) surfactants, a new class of surfactants specifically tailored for the use of μ E's in organic synthesis. They contain functional groups which allow them to be employed for catalysis of a given reaction and then to be cleaved to nonsurfactant products prior to workup. As a result, potentially serious surfactant-derived emulsion problems in liquid-liquid extractions of workup are avoided entirely. We also began the design and synthesis of turnover catalysts for carbon and phosphorus ester hydrolysis. A turnover system functions as a true catalyst by participating in more than one hydrolytic event.

II. Statement of the Most Important Results

In the first part of the project we studied several reactions of water-insoluble organic substrates with water-soluble inorganic reagents. The reactions of benzyl chloride (1a) and two para-substituted analogues (1b and 1c) with Br^- (eq 1) were performed in various μ E's composed of hexadecyltrimethylammonium bromide (HTABr), 1-butanol, hexane, and $\text{KBr-H}_2\text{O}$.¹ The μ E's generally solubilized more 1 than, and gave pseudo-first-order rate constants (Br^- in excess) for the initial portion of the reaction comparable to aqueous micellar HTABr and $\text{H}_2\text{O-C}_2\text{H}_5\text{OH}$ solutions. Furthermore, with



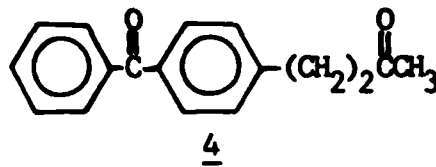
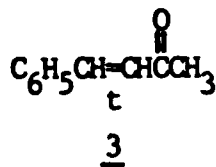
a, R = H

b, R = C₂H₅

c, R = n-C₁₂H₂₅

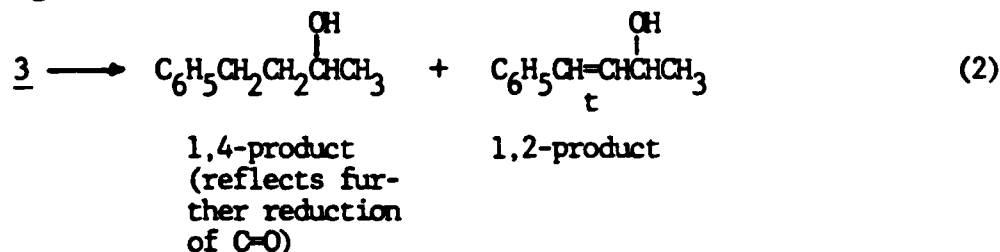
extended reaction times the conversions of 1a to 2a were greatest in the (water-rich) μ E's. Thus, for synthetic purposes, μ E's were preferable to the other two media. The μ E pseudo-first-order kinetic data suggested that the interphase was the predominant reactive site with little, if any, contribution from the oil pseudophase via a phase transfer mechanism. The aqueous pseudophase was discounted as a significant reactive site because the substrates 1 have limited solubility in water. The second-order rate constants for reaction in the μ E interphase calculated by the method of Bunton and de Buzzaccarini² were comparable to those for the micellar pseudophase of aqueous HTABr and for H₂O-C₂H₅OH. Thus, there appeared to be no unusual kinetic feature of the μ E reactions.

The reductions of several mono- and dicarbonyl compounds with BH₄⁻ were carried out in μ E's composed of HTABr, 1-butanol, hexane, and NaBH₄-KOH-H₂O.³ Relative to 2-propanol-H₂O mixtures, the μ E's did not provide any substantial kinetic advantage. The interphase was again implicated as the reactive site. Studies of regioselectivity control were made with enone 3 and diketone 4.

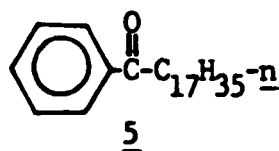


With the former, modest amounts of and no 1,4-reduction (eq 2) were obtained in the μ E's and 2-propanol-H₂O mixtures, respectively, along with predominant

1,2-reduction. With latter, the reactivity of the aromatic carbonyl group relative to that of the aliphatic carbonyl group increased on going from 2-propanol-H₂O to μ E media. This increase was perhaps due to the definite

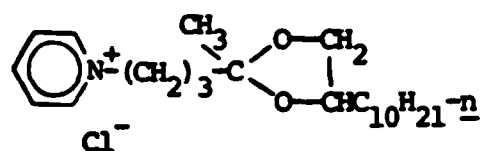


possibility that the aromatic carbonyl group prefers the interphase as a solubilization site more so than does the aliphatic carbonyl group. The oil-rich μ E of the study was especially appropriate for the homogeneous reduction of lipophilic ketone 5. In the 2-propanol-H₂O mixtures and even in the other μ E used this material was insoluble.

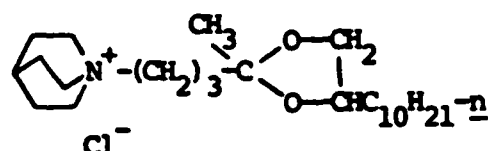


Overall, the results of the two studies above indicated that μ E catalysis is certainly competitive with phase transfer catalysis with respect to rate and conversion. Product isolation from μ E's can present problems, however. In each study a preparative run was made, and product isolation involved precipitation of HTA⁺ with a hydrophobic counterion, ClO₄⁻ in the former and PF₆⁻ in the latter. Filtration and extractions then followed to give recoveries of 61% and 93%, respectively. Thus, cumbersome procedures were necessary, and uniformly high recoveries were not obtained. The practical application of μ E catalysis therefore will require simplified and more efficient product isolation methodology, which destructible surfactants can provide.

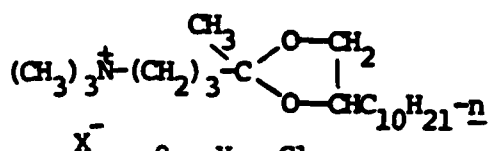
The first examples of destructible surfactants for application in organic synthesis were prepared and characterized.⁴⁻⁶ Systems 6-8 are based on a ketal group, which is stable under neutral and basic conditions but is hydrolyzed under acidic conditions as illustrated with 8 (eq 3). System 9 is based on an appropriately substituted Si-O bond, which is stable over the pH



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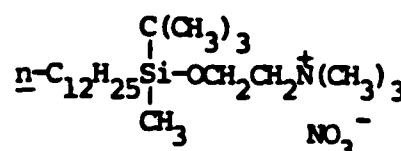
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8a, X = Cl

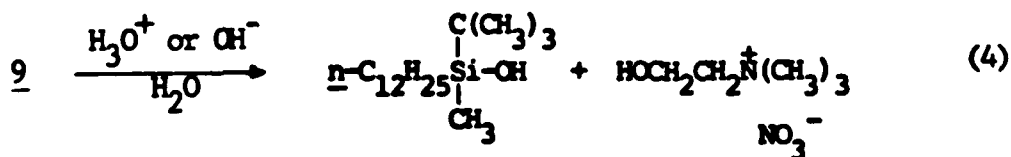
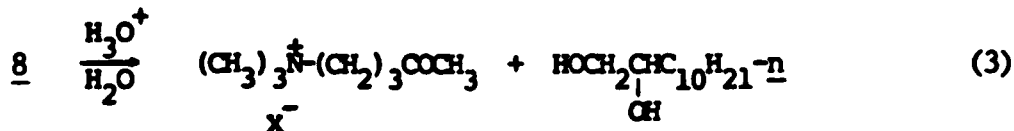
b, X = Br

c, X = OSO₂CH₃



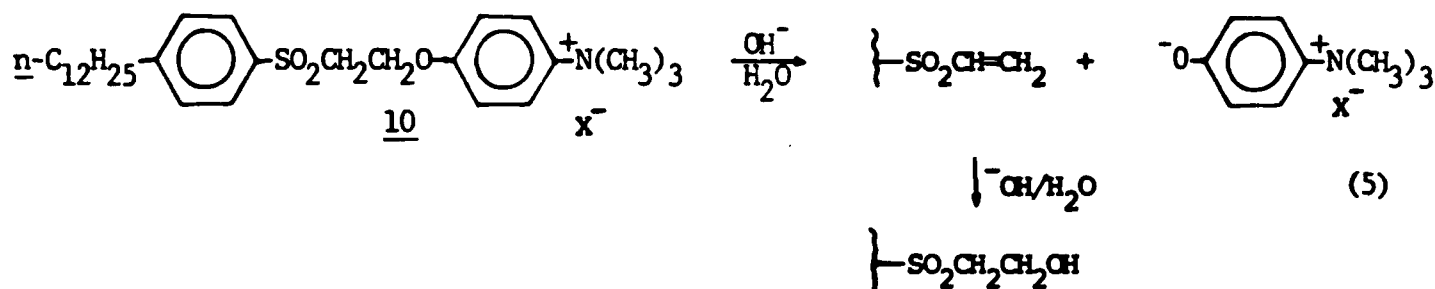
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range 3-11 but hydrolyzes on either side as shown (eq 4). Therefore, in general, cleavage of a destructible surfactant separates its major lipophilic and hydrophilic portions with resultant formation of nonsurfactant products which do not cause emulsion problems in extractive workups. All of these destructible systems had critical micelle concentrations typical of cationic



surfactants, and the catalytic abilities of 6, 7, and 9 in several reactions under micellar/emulsion conditions were comparable to those of HTABr. We also

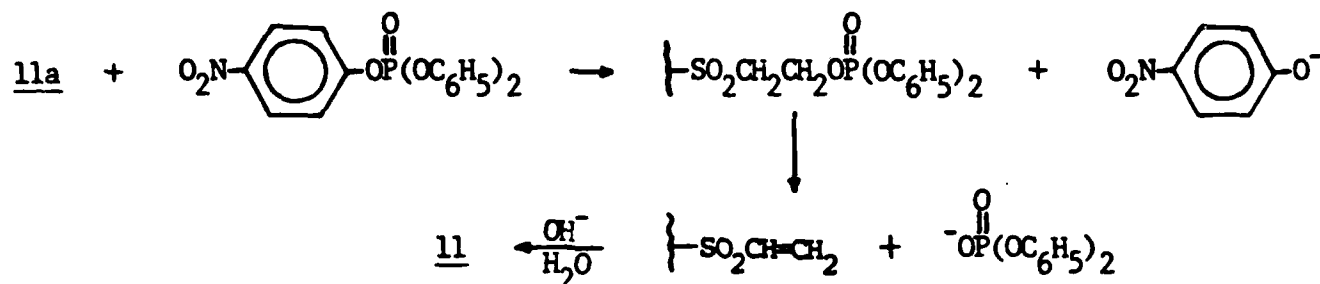
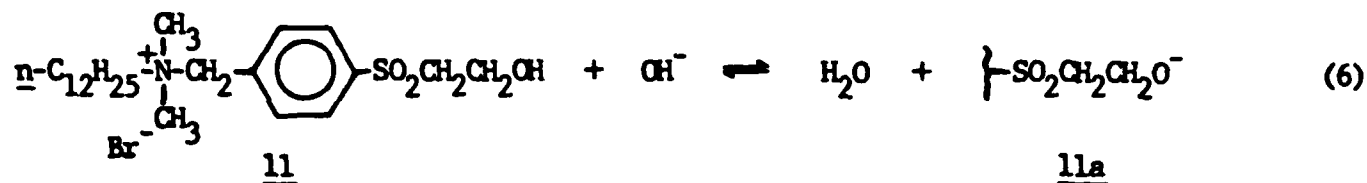
prepared destructible surfactant 10 but have not characterized it yet. It should be stable under acidic and neutral conditions but undergo E1cB cleavage under even mildly basic conditions as illustrated (eq 5). The use of destructible surfactants does have a complication. The desired organic



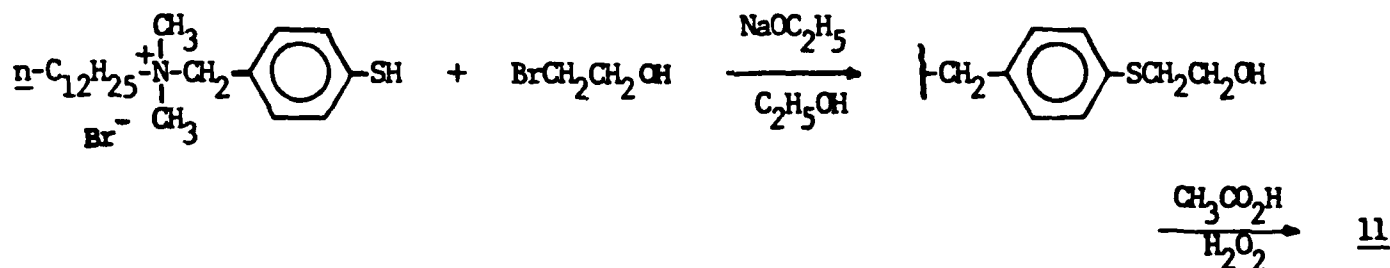
compound must be separated from the cleavage products of the surfactant. An acidic or basic compound would be separated by appropriate extractions with acid and base. The isolation of a neutral compound would require separation from the neutral cleavage product by a method such as distillation or chromatography.

We have formulated μ E's from 8a, b, and c in combination with 1-butanol, hexane, and 0.01 M NaHCO₃.⁷ The optimum 8 to 1-butanol (cosurfactant) ratio was determined so that the microemulsion region in the pseudoternary phase diagram was maximized. In general, such an optimized system will be better suited for organic synthesis than one with a smaller one-phase region. With the former, it is more likely that a solution will be found that will solubilize the requisite amounts of both substrate and reagent without phase separation, as well as yield the desired reactivity.

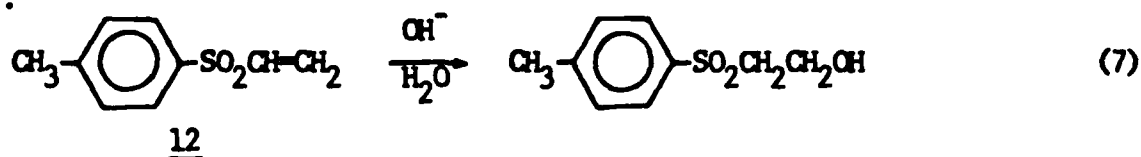
In other work we attempted the synthesis of functionalized surfactant 11. This compound was considered a potential turnover catalyst⁸ for carbon and phosphorus ester hydrolysis as illustrated with p-nitrophenyl diphenyl phosphate (eq 6). The synthetic pathway we followed was unsuccessful,



presumably because of the lability of the benzyl position in the final steps shown. From this experience it is clear that in the preparation of a functionalized surfactant, the surfactant character should be generated as



late as possible in the synthetic scheme. Other work with model compound 12 indicated that 11 probably would not have functioned as a turnover catalyst anyway. The rate of Michael-like addition of water to 12 (eq 7) was very slow.



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1. Refs. 3 and 8 of Section III. below.
2. C. A. Bunton and F. de Buzzaccarini, J. Phys. Chem., **86**, 5010 (1982).
3. Ref. 6 of Section III.

4. Ref. 1 of Section III.
5. Ref. 2 of Section III.
6. Ref. 7 of Section III.
7. Ref. 5 of Section III.
8. For a recent example, see R. A. Moss, K. W. Alwis, and J.-S. Shin, J. Am. Chem. Soc., **106**, 2651 (1984).

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2. D. A. Jaeger and M. D. Ward, "Destructible Surfactants Based on a Silicon-Oxygen Bond", J. Org. Chem., **47**, 2221-2223 (1982).
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